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Thermoelectric Characteristics of a Commercialized Mg_2Si Source Doped with Al, Bi, Ag, and Cu

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The thermoelectric characteristics of commercial polycrystalline Mg_2Si doped with Bi, Al + Bi, Ag, and Cu were examined. The samples for the thermoelectric measurements were prepared using the plasma-activated sintering (PAS) technique. The measured values of the Seebeck coefficient were compared with values calculated using the all-electron band-structure calculation package (ABCAP) based on a full-potential augmented-plane-wave (FLAPW) band-structure calculation in a local density approximation (LDA). For the Bi + Al-co-doped samples, the observed values of the dimensionless figure of merit, ZT, were higher than those of solely Bi-doped samples. The maximum value obtained for Bi + Al-doped Mg_2Si was 0.77 at 862 K. For the Ag-doped samples, ZT was significantly lower than that of the Bi + Al-doped samples, with the maximum value being about 0.11 at 873 K.

Key words: Thermoelectrics, Mg_2Si, environmentally-benign, doping, Bi, Al, Ag, Cu, ABCAP, Seebeck coefficient, electrical conductivity, power factor, thermal conductivity, ZT

INTRODUCTION

The environmentally-benign material Mg_2Si has been identified as a high-performance thermoelectric material in the temperature range from 500 K to 800 K. In order to realize a practical thermal-to-electric (TE) device, impurity doping with appropriate elements is needed to enhance TE performance and ensure stable operation at elevated temperatures. It is known that Bi doping is effective in improving the thermoelectric performance of n-type Mg_2Si.[1] However, there is concern regarding the possibility of restrictions on Bi as a hazardous substance; accordingly we have attempted to introduce nontoxic Al as a substitute n-type impurity in Mg_2Si. For the p-type impurity, Ag seems to be the exclusive candidate.[2]

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We report on the temperature-dependent thermoelectric properties of Mg_2Si, doped with impurities (Bi, Al, Ag, Cu), prepared by plasma-activated sintering. For the starting material, commercial polycrystalline Mg_2Si fabricated by Union Materials was used. The ZT values obtained for Bi + Al/Mg_2Si were comparable to those for Bi/Mg_2Si. The highest ZT value achieved for Bi/Mg_2Si was 0.64 at 860 K, while for co-doped Bi + Al/Mg_2Si a value of 0.77 was observed at 860 K. Although the ZT values for Ag/Mg_2Si exhibited temperature-dependent compensation and lower values than that of the n-type specimens, definite p-type characteristics were observed.

EXPERIMENTAL PROCEDURES

Commercial polycrystalline Mg_2Si fabricated by Union Materials was used in the present experiments. Dopants Al, Bi, Ag, and Cu were

Table I. Fabricated samples with their doping concentrations

Sample Name	Concentration			
	Al (at.%)	Bi (at.%)	Ag (at.%)	Cu (at.%)
MS-Bi1	–	1.0	–	–
MS-Bi2	–	2.0	–	–
MS-Al1Bi1	1.0	1.0		
MS-Al2Bi1	2.0	1.0		
MS-Ag1			1.0	
MS-Ag3			3.0	
MS-Cu1	–	–		1.0

Table II. Hall concentration and Hall mobility of the grown samples at room temperature

Sample	Conductivity	Hall Carrier Conc. (cm^{-3})	Hall Mobility (cm^2/Vs)
MS-Bi1	*n*	1.5×10^{20}	81.9
MS-Bi2	*n*	1.4×10^{20}	74.8
MS-Al1Bi1	*n*	1.8×10^{20}	64.8
MS-Al2Bi1	*n*	1.4×10^{20}	80.6
MS-Ag1	*p*	7.4×10^{17}	31.3
MS-Ag3	*p*	1.1×10^{18}	24.7
MS-Cu1	*n*	–	–

incorporated into the Mg_2Si sources during synthesis. The polycrystalline Mg_2Si was pulverized to powder with size of 75 μm or less and then sintered by a plasma-activated sintering (PAS) technique using an ELENIX PAS-III-Es. The fabricated specimens are listed in Table I with the dopant concentration. For some samples Bi and Al were doped simultaneously. For the PAS method, a graphite die filled with Mg_2Si powder was processed at 1123 K for 10 min at a pressure of 29.4 MPa with a heating rate of 100 K/min. The samples were then cut using a wire saw. The fabricated samples had sufficient density, and there was no precipitation of highly conductive material, such as Mg or Si. The thermoelectric properties, that is, the Seebeck coefficient, S, and the electrical conductivity, σ, were measured using ULVAC-RIKO ZEM-2 equipment, and the thermal conductivity, κ, was measured using a laser flash method with an ULVAC-RIKO TC-7000H device over a temperature range from room temperature to 860 K. The dimensionless figure of merit, ZT, was then estimated. The Hall carrier concentration and Hall mobility were measured at room temperature using the van der Pauw method. The magnetic flux density was 0.53 T, and the current was 100 mA. A full-potential augmented-plane-wave (FLAPW) band-structure calculation in a local density approximation (LDA) was carried out for Mg_2Si using the all-electron band-structure calculation package (ABCAP).[3,4] The Seebeck coefficients were estimated using the calculated band structures with varied carrier concentrations.

RESULTS AND DISCUSSION

The results of the room-temperature Hall measurements are summarized in Table II. Bi and Al are well-known impurities which act as donors in Mg_2Si, while Ag acts as an acceptor. In the case of Cu the observed S values were negative for the measured temperature range, indicating n-type conductivity, although Cu belongs to the group XI metals like Ag. For Mg_2Si doped with Bi, no distinct increase in Hall carrier concentration was observed when the Bi incorporation was increased from 1 at.% to 2 at.%. One report puts the empirical limit of the solid solubility of Bi in Mg_2Si as high as ~0.4 at.% when grown by the vertical Bridgman crystal growth process.[5] Synthesis of the present commercial Mg_2Si source is provided by an all-melt technique, which has comparable reaction conditions, i.e., process temperature, reaction duration, and initial source loading, to those of Fukano, thus the expected solid solubility limit for Bi is likely to be less than 1 at.%. On the other hand, Bi doping concentrations of more than ~2 at.% have been acknowledged as being preferable for obtaining low thermal conductivity resulting in ZT values approaching unity for samples prepared using the growth technique.[5]

Figure 1 shows the temperature dependence of the measured S values together with the values calculated using the ABCAP code for (a) n-type and (b) p-type specimens. For the ABCAP calculations, the temperature-dependent bandgap, E_g, which is expressed by the relationship $E_g = E_{g0} + \beta T$, where $E_{g0} = 0.78$ eV and $\beta = -5 \times 10^{-4}$ eV/K, was used, and E_g was estimated to be 0.63 eV at room temperature.[6,7] Regarding the Bi-doped and Bi + Al-co-doped specimens, the ABCAP calculations showed good fits for temperatures up to ~700 K, which corresponds to the extrinsic region. By means of the fitted parameters over the observed S values, the estimated values of the net carrier concentration, $N_D - N_A$, for the MS-Bi1 and MS-Al1Bi1 samples is estimated to be 1.8×10^{20} cm^{-3}, which is close to the result of the Hall measurement. On the other hand, the estimated $N_D - N_A$ values from the ABCAP fitting for the MS-Bi2 and MS-Al2Bi1 samples show slightly smaller values. The observed S values as a function of temperature for MS-Bi1 and MS-Bi2 have some differences; however, they are marginal, possibly indicating moderate or rather less electrical activation of incorporated Bi atoms in MS-Bi2 than in MS-Bi1.

For Cu-doped Mg_2Si, the reproducibility of the measurement results were acceptable, i.e., repeated

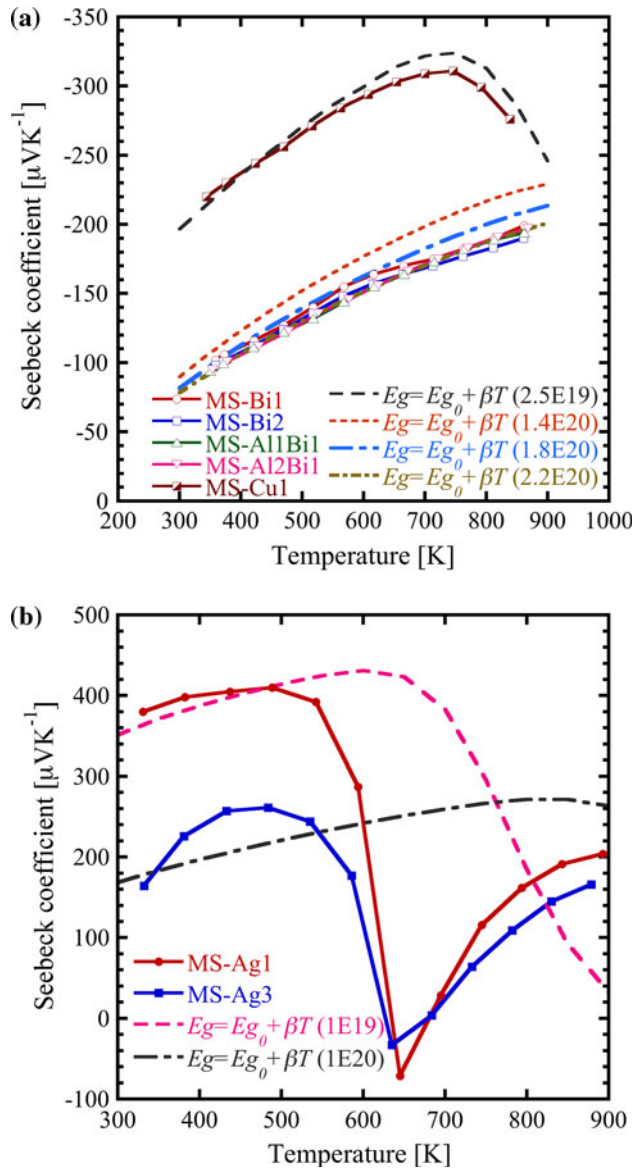

Fig. 1. Measured Seebeck coefficients and curves of the calculated Seebeck coefficients fitted using ABCAP for (a) *n*-type and (b) *p*-type.

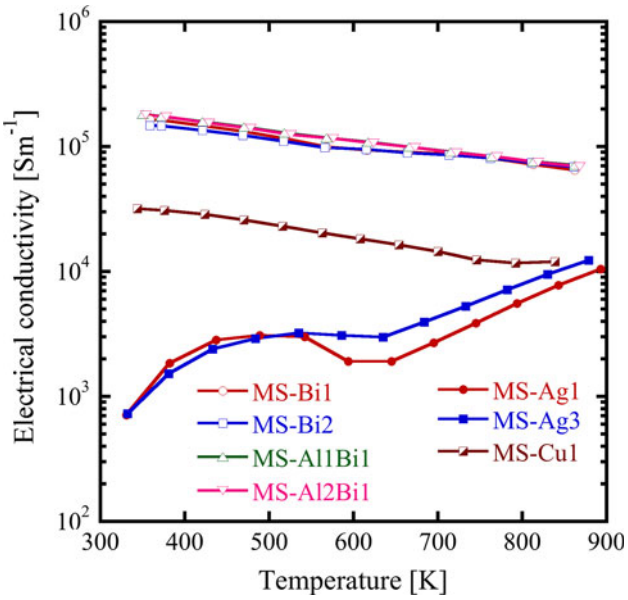

Fig. 2. Temperature dependence of the electrical conductivity.

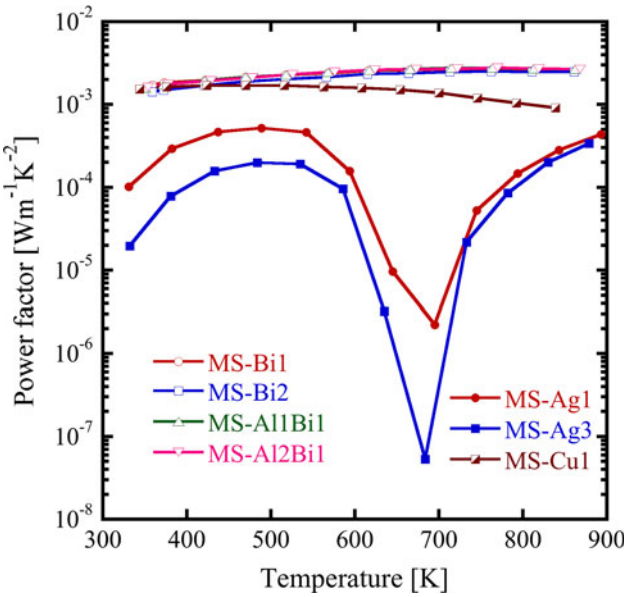

Fig. 3. Temperature dependence of the power factor, $S^2\sigma$.

heating/cooling measurements on identical samples at elevated temperatures as high as 900 K showed comparable values of Seebeck coefficient and electrical and thermal conductivities. However, it is noted that the results of the S measurements were not reproducible, i.e., the observed S values fluctuated in certain ranges even under the same doping concentration. The data plotted for the Cu-doped sample in Fig. 1 form a representative curve showing the dominant tendency observed for initial Cu concentrations of the order given. The carrier concentration estimated using the ABCAP calculation seems to be one order of magnitude smaller than the expected value of the order of $\sim 10^{20}$ cm^{-3}, which is simply referred the incorporated initial Cu concentration.

For Ag-doped Mg_2Si, reproducibility of the synthesis and measurement results was observed. The Ag-doped samples, MS-Ag1 and MS-Ag3, exhibited positive S values over a major portion of the temperatures at which they were measured, indicating *p*-type conductivity, while they drop rapidly from about 550 K and exhibit conductivity type conversion at temperatures between 600 K and 700 K. It is seen that the estimated carrier concentrations, $N_A - N_D$, are much smaller than the measured Hall carrier concentrations. In the case of samples prepared by the vertical Bridgman growth method, the

S characteristics as a function of doping concentration and temperature agree well with the ABCAP calculations.[3] However, in the present case, the agreement between calculation and experiment is poor, as shown in Fig. 1b. The reason for the observed discrepancy is still unclear, and a supplementary investigation is underway.

The observed S values of Ag-doped specimens were positive below 550 K, then become negative between 600 K to 700 K, which is associated with the onset of intrinsic behavior. After that, the S values recover to positive values for temperatures above 700 K. The present samples contain relatively high concentrations of process-induced residual Al, thus the onset of intrinsic behavior was shifted toward low temperature. Since it is known that Mg-related structural defects exhibit donor-like behavior, as shown by a first-principles calculation,[8] this may have an influence on the characteristics of the Ag-doped p-type Mg_2Si, such as carrier compensation over the whole temperature range.

Figure 2 shows the variation in the temperature dependence of σ. It seems that the observed characteristics signify that Bi-doped and Bi + Al-co-doped Mg_2Si have good properties. As the sample temperature is increased, the σ values decrease at all temperatures for Bi-doped and Bi + Al-co-doped samples. The values of σ exhibit a reasonable variation in their temperature-dependent characteristics, corresponding to the observed S values. For the Bi + Al-co-doped sample, the influence on the σ values due to Al co-doping gave

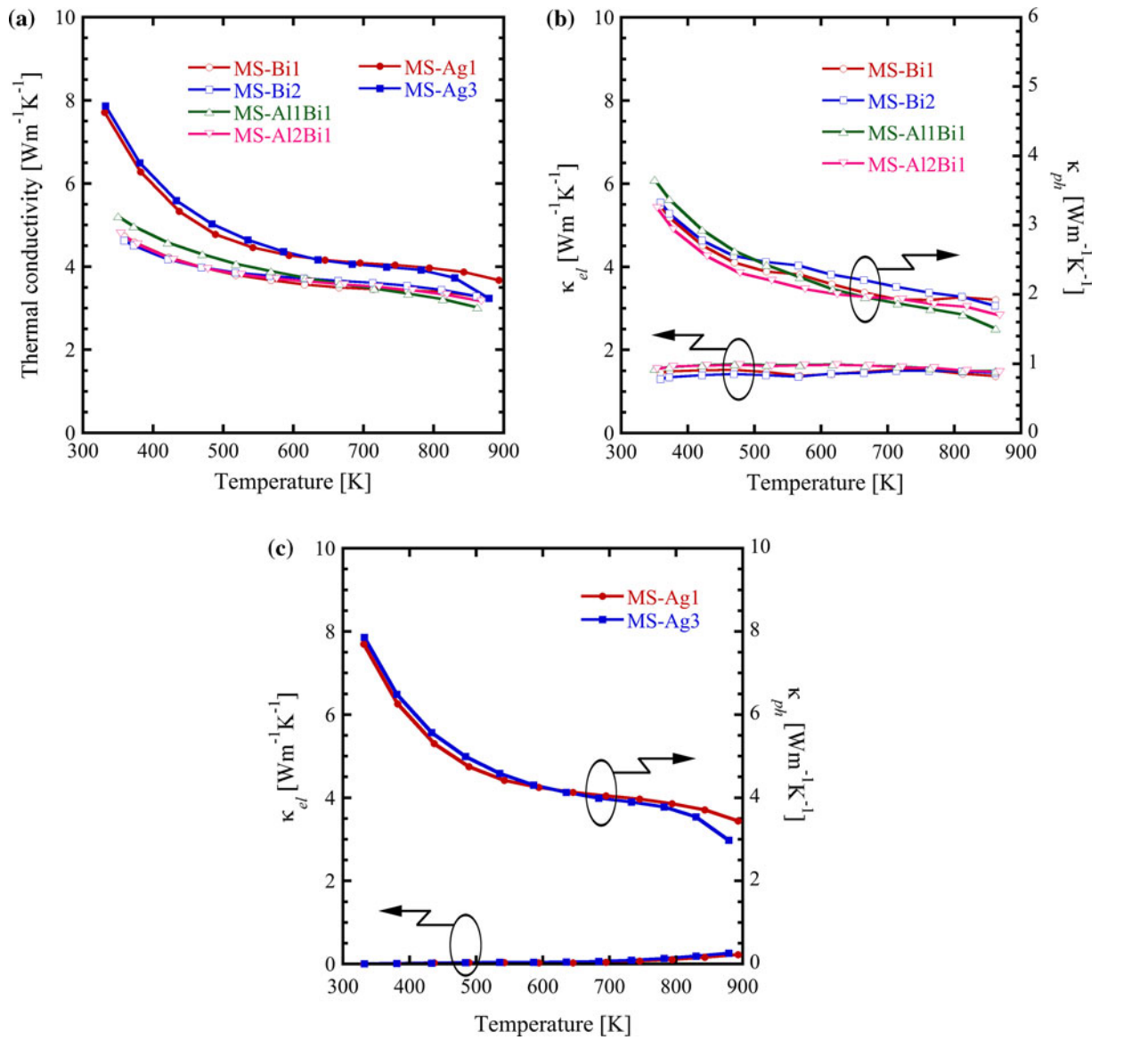

Fig. 4. The thermal conductivity of samples doped with Bi, Bi + Al, and Ag in the temperature range from 350 K to 873 K: (a) total κ, and (b) electronic component κ_{el} and lattice component κ_{ph} of n-type samples; (c) κ_{el} and κ_{ph} of p-type samples.

rise to a slight improvement over the whole temperature range. However, no remarkable difference was observed in the magnitudes of the S and σ values. The MS-Ag1 and MS-Ag3 samples exhibit a significant drop, seemingly due to carrier compensation at ~600 K to mid-700 K, which can be associated with the effect of donor-like Mg-related structural defects and process-induced residual Al donor impurities.

Lower σ and higher S values observed for MS-Cu1, as compared with Bi- or Bi + Al-doped samples, possibly suggest the occurrence of some compensation due to a low level of incorporated acceptor atoms. In our present experiments, there is a hint of carrier compensation owing to the amphoteric behavior of Cu, which is also correlated with the fabrication process parameters. In order to understand the observed behavior of Cu, more systematic investigation of the solid solubility of Cu in Mg_2Si and verification of the likelihood of amphoteric characteristics are required.

Figure 3 shows the temperature dependence of the power factor, $S^2\sigma$. Except for the Cu-doped specimen, Bi-doped and Bi + Al-co-doped specimens present a flat characteristic over the anticipated operational temperature range of 600 K to 800 K, with values from $\sim 2 \times 10^{-3}$ W/mK^2 to 3×10^{-3} W/mK^2. No remarkable difference is seen in the Bi- and Bi + Al-doped samples at elevated temperatures. For the Cu-doped specimen, a considerable decrease at elevated temperature is observed. With regard to the Ag-doped p-type specimens, MS-Ag1 and MS-Ag3, low values and a large variation are indicated.

The temperature-dependent κ values for undoped and doped specimens are shown in Fig. 4. The observed thermal conductivities are separated into contributions from the lattice (κ_{ph}) and electronic (κ_{el}) components. By means of the Wiedemann–Franz law, the κ associated with the electronic component was calculated from the relation $\kappa_{el} = L_0\sigma T$, where L_0 is the Lorentz number, 2.45×10^{-8} V^2/K^2.[9] As shown in Fig. 4a, the observed total κ values decrease monotonically with increasing sample temperature up to ~723 K, indicating an increase in phonon scattering, and start to level out to 3 W/mK to 4 W/mK beyond ~600 K. It is seen that co-doping Mg_2Si with Bi + Al brought about a slight decrease in the κ_{ph} values over the anticipated operational temperature range, with comparable temperature dependences to those of Bi-doped samples, as shown in Fig. 4b. Since the thermal conductivity behavior of the Bi + Al-co-doped samples, MS-Al1Bi1 and MS-Al2Bi1, is similar to that of Bi-doped Mg_2Si beyond ~700 K, thus ensuring a similar temperature gradient for practical device operation at elevated temperatures, and since Al is a benign material compared with Bi, Al is a good substitute for Bi. For MS-Ag1 and MS-Ag3, the observed κ_{ph} values were larger than those of Bi- and Bi + Al-doped samples over the whole temperature range, and the κ_{el} values were much smaller, as was observed in the σ results.

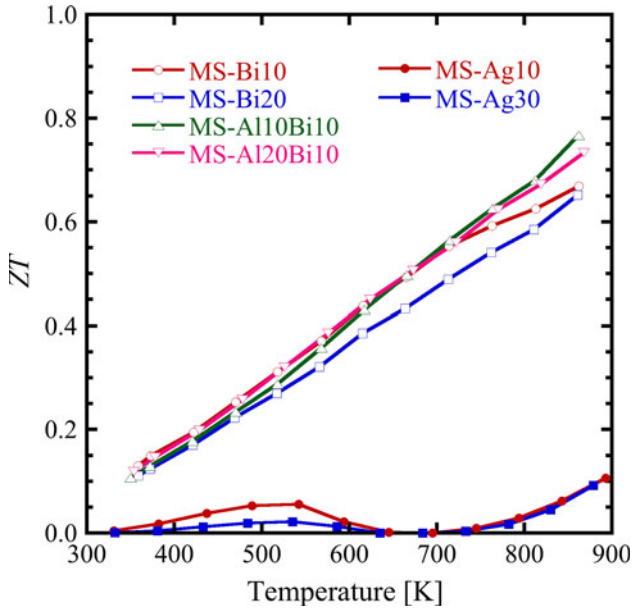

Fig. 5. Dimensionless figure of merit ZT.

Figure 5 shows the values of ZT for Bi-, Bi + Al-, and Ag-doped samples. The maximum values obtained for Bi + Al-doped Mg_2Si are 0.77 at 862 K (MS-Al1Bi1) and 0.74 at 862 K (MS-Al2Bi1). It is seen that the values for the Bi + Al-doped samples are higher than those of the Bi-doped samples, MS-Bi1 and MS-Bi2, indicating that supplemental Al incorporation seems to be a good approach for Bi-doped Mg_2Si, and also helps reduce the use of toxic Bi by using Al as an alternative. For the MS-Ag1 and Ms-Ag3 samples, the ZT values are significantly lower than those of the Bi + Al-doped samples, due to the decrease in the Seebeck coefficient above 600 K; the maximum value is about 0.11 at 873 K.

CONCLUSIONS

The thermoelectric characteristics of Mg_2Si doped with Bi, Al + Bi, Ag, and Cu were examined using commercial Mg_2Si source material produced by Union Materials. The Seebeck coefficient and the electrical and thermal conductivities of samples fabricated using a plasma-activated sintering technique were measured. Supplemental Al incorporation with Bi doping in Mg_2Si resulted in higher ZT values than those of solely Bi-doped specimens over the anticipated operational temperature range. It seems that Bi + Al doping is a good alternative to Bi-doped Mg_2Si, and reduces the use of toxic Bi by using Al as an alternative to Bi. Ag doping of the Mg_2Si source material was inadequate for realizing p-type thermoelectric behavior for practical use in thermal-to-electric conversion. Cu doping was unstable, and some tentative evidence of amphoteric characteristics was observed.

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